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Procedia Engineering 53 (2013) 354 – 361

Procedia Engineering

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Malaysian Technical Universities Conference on Engineering & Technology 2012, MUCET 2012
Part 1- Electronic and Electrical Engineering

The SEM & AFM Images of MEH-PPV Films below CLA Region

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Abstract

Poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is an example of conducting polymer that used to fabricate an organic light emitting diode (OLED). The surface roughness and homogeneity of MEH-PPV film is then investigated by using Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM). The luminescence of the device was effect by the surface roughness of the film. The standard spin coating technique is used to produce uniform thin film onto large area. MEH-PPV can be easily dissolved in non-aromatic (chloroform) and aromatic (toluene) solvents to exhibit different optical, structural and electrical properties. The MEH-PPV solutions in the two types of solvents were prepared at solution concentration of 1 $mgml^{-1}$ to 8 $mgml^{-1}$ and 1 $mgml^{-1}$, 5 $mgml^{-1}$ and 8 $mgml^{-1}$in chloroform and toluene respectively. There are three regimes derived from the viscosity measurement. These regimes are measured related to concentration of loose aggregation, (CLA). The regime are c<CLA, c>CLA and c>CLA. The MEH-PPV solutions used in this work is classified in the regime of c<CLA. In this regime, the structural properties of MEH-PPV film are independent on the spun speed, thickness and solution concentration for the two type of solvents used in preparing the polymer films.

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Keywords: *MEH-PPV; CLA; non-aromatic & aromatic solvents; AFM and SEM images.*

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1. Introduction

Poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is an electroluminescent polymer, widely utilized in the fabrication of Organic Light Emitting Diodes (OLEDs). MEH-PPV has the advantage of being easy to dilute in volatile solvent such as aromatic (chlorobenzene, toluene) and non-aromatic (THF, chloroform) solvents because of the polymer chains having alkoxy on phenyl group. In addition, another advantage of using MEH-PPV as electronic materials is due to low cost processing. Many techniques can be used to fabricate OLED such as Langmuir-Blodgett, self assembly, thermal evaporation, ink-jet printing, dip-coating and physical vapour deposition (PVD) technique. In this work, spin coating technique is chosen to produce uniform thin film onto large area. This is a common technique used in fabricating device as it produces homogeneous film. This paper presents series of experiments designed to study the morphological effect of conjugated polymer due to the final physical properties of the films and device. The conjugated polymer is strongly affected by the film morphology because when the π-electron of two conjugated polymer segments are in contact, there is a significant electronic interaction between them [1]. Conjugated polymer has their own unique morphology which is strongly influenced by processing conditions. There are several parameters regarding to the polymer processing condition such as the type of solvent, spin coating speed, solution concentration and annealing temperature [1-4]. These conditions are important factors in determining the final physical properties of the polymer thin films, the final morphology of the film and

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Selection and peer-review under responsibility of the Research Management & Innovation Centre, Universiti Malaysia Perlis
doi:10.1016/j.proeng.2013.02.046

subsequently the performance of the device made from the polymer. The focus on this study is to investigate the relation between spin speed, concentration of solution and type of solvent on the performance of the device. Initially, the polymer was diluted in the concentration range from 1 to 8 $mgml^{-1}$. It must be noted that the morphology of the films are dependent on the spun speed, concentration of solution and the type of solvent used. However this effect is only prominent if the working regime of the polymer solution concentration is in the regime of concentration of loose aggregation (CLA). However, in this work, the investigation is carried out in the regime of c<CLA. The reason is, we are interested to evaluate the effect of polymer interactions due to the structural, optical and electrical properties of the MEH-PPV prepared by spin coating technique where the emission spectrum of the polymer in the region is dominated by single excited state which enhances high PL efficiency and reduced inter-chain interaction. There are several interesting results on the morphology of the films that can be seen especially from the AFM images. The polymer film can be clearly seen forming several aggregations. Interest in this regime can be seen as a new phenomena effect on the performance of the films and device. It is also known that concentration of solution is always dependent on the molecular weight of polymer. Thus the value of concentration in CLA regime of each polymer is not the same.

2. Material and Method

The red color, MEH-PPV used in this work was purchased from H.W. Sands with purity of > 99%. The molecular weight of the MEH-PPV is 200,000Mw (PS standard). The material was dissolved in non-aromatic solvent (chloroform) and aromatic (toluene) at solution concentration of 1 $mgml^{-1}$ to 8 $mgml^{-1}$. The MEH-PPV was then coated onto glass substrate and indium tin oxide (ITO) with spin speed ranging from 1k rpm to 6k rpm for 10 seconds. The thickness range of MEH-PPV film using toluene solution are ~550±28 nm to 45±2 nm while that film prepared using chloroform, the thickness range are ~490±25 nm to 65±3 nm, depending on spin speed. The sample dried in vacuum chamber at 40°C for 2 hour. Next, to check the roughness of the films, Atomic Force Microscope (AFM) was used with scanning area of (20 × 20) μm^2 and (7 × 7) μm^2 . Finally the morphology of the MEH-PPV thin films sample is carried out by using Scanning Electron Microscope. (SEM). Scanning range was varied at different position to inspect different pattern from the films surface.

3. Result and Discussion

Figure 1 shows the SEM images of the MEH-PPV thin films on several different substrates spin-coated at speed 1k rpm. Figure 1 A i), B i), and C i) represent the images of MEH-PPV films prepared from chloroform deposited onto metal Indium Tin Oxide (ITO), silicon and glass substrate respectively with the resolution of 10 µm. Figure 1 A ii), B ii) and C ii) show the same images with higher resolution, 400 nm. From the results shown it can be seen that polymer coated onto different substrates reveals different patterns. The MEH-PPV polymer films are much more homogenous when coated onto glass substrate compared to ITO and silicon. The images of the films show that the films are homogenous without void and crack [5]. At lower resolution, it can be seen that the film on the ITO substrate is homogenous. However when the resolution is higher, the film on the ITO substrate looks inhomogeneous. There seems to be some bubble patterns on the polymer films. There are also some irregular objects on the polymer film coated on silicon wafer substrate as shown in Figure 1 B i). The irregular object seen on the left side of the polymer film image is probably a dust particle or other impurities as also reported in reference [4]. Other regions on the centre of the same substrate which can be seen in 4.6 B (i), when the scanning resolution was set at 400 nm; shows no such features.

Figure 2 shows the SEM images of the MEH-PPV film coated onto ITO substrate with solution concentration of 8 $mgml^{-1}$. The images were taken by several scales resolution. At the scale of 20 µm the vicinity of the surface is homogenous, no such irregular objects are observed, and the layer is essentially flat. However, when the scale is increased to 5µm, the distribution of irregular objects is significantly observed which maybe due to polymer clumping. The polymer layer tends to aggregate when the solution concentration increases. The aggregation is caused by the agglomeration of the coiled chains [4] which is clearly observed in the image obtained at resolution scale 500 nm in Figure 2. Figure 3 shows (20 × 20) μm^2 atomic force microscopy image of a cleaned ITO substrate. The color changes from dark brown to light brown represent a height difference of 0.91 nm. The σ (RMS) value of this ITO is smaller compared to that reported in reference [6] which is 2.781nm. The irregular objects seen in the circles drawn in the 2D images (a) can also be seen as protruding objects in the 3D image (b). The irregular objects are the dust particles which only exist on certain area of otherwise flat and homogeneous surface.

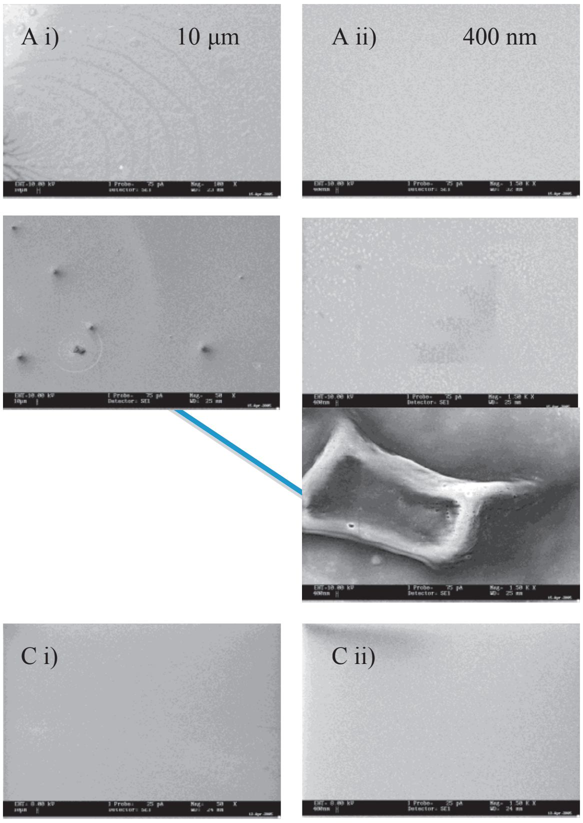
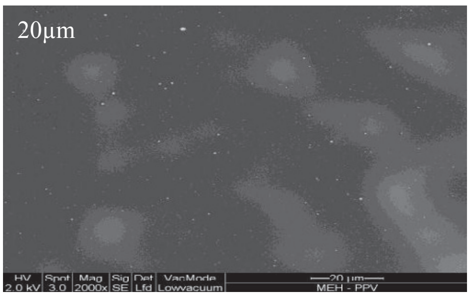


Fig. 1. 10µm and 400 nm scales resolution of SEM images of MEH-PPV films prepared from $1 mgml^{-1}$ chloroform solution at 4k rpm spun speed by using different substrate. Figure A) ITO, B) silicon and C) glass substrates.

The ITO image was taken such that comparison can be made with the ITO coated with the MEH-PPV layer as shown in Figures 4, 5, 6 and 7. Figure 4 to 7 show Atomic Force Microscope (AFM) images of the MEH-PPVPPV spun film coated onto ITO substrate from chloroform solution with concentration of $8 mgml^{-1}$ but at various spin speed. The scanning area is maintained at (2×2) μm^2. The 2D images and 3D images are shown in the (a) and (b) figures respectively. The color changes of the images is from dark brown to the light brown which represents the height difference of [7,8] ~1.5 nm. The polymer aggregation on the film surface is evident by the dark brown and light brown surfaces observed from the images [1]. In this work, $8 mgml^{-1}$ is the highest solution concentration used to produce MEH-PPV layer on ITO coated glass substrate. The effect of spin speed variation on the surface morphology of the MEH-PPV is investigated from the AFM images obtained. The aggregation of the films and the polymer clustering or clumping are visible in the range of few-hundred nanometers high at higher concentration [9].



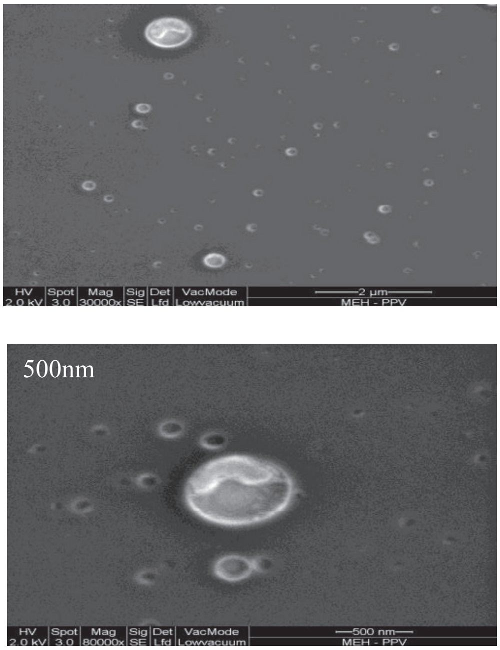


Fig. 2. The SEM images of 8 mgml^{-1} concentration MEH-PPV spun film on ITO electrode with three resolutions

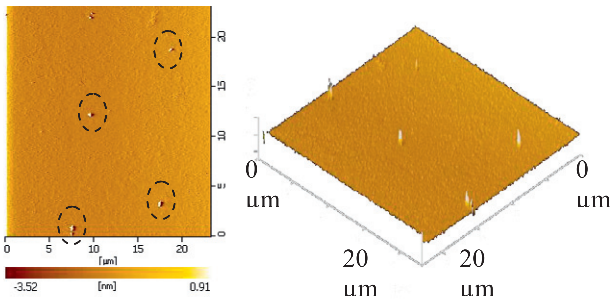


Fig. 3. 2D and 3D images of 20 µm × 20 µm AFM images of cleaned ITO substrate

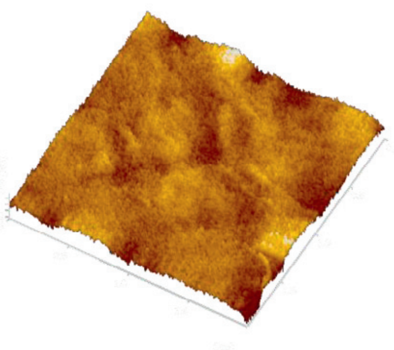


Fig. 4. 2µm ×2µm AFM images of MEH-PPV film spun at 1k rpm speed with solution concentration of 8 mgml^{-1}.

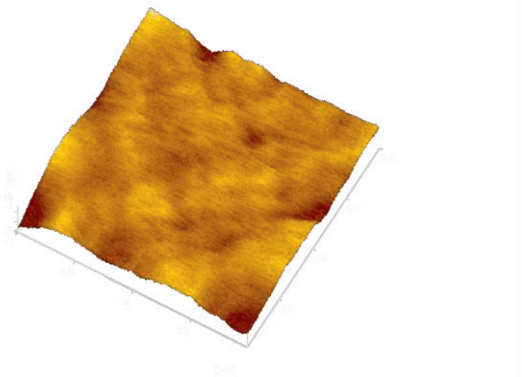


Fig. 5. 2μm ×2μm AFM images of MEH-PPV film spun at 3k rpm speed with solution concentration of 8 $mgml^{-1}$.

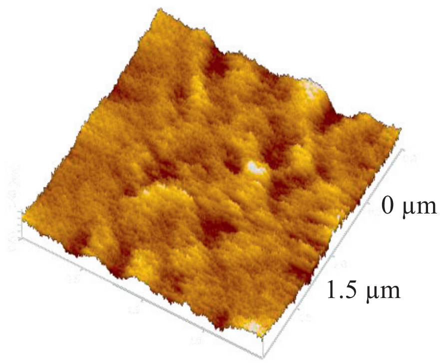


Fig. 6. 2μm ×2μm AFM images of MEH-PPV film spun at 4k rpm speed with solution concentration of 8 $mgml^{-1}$.

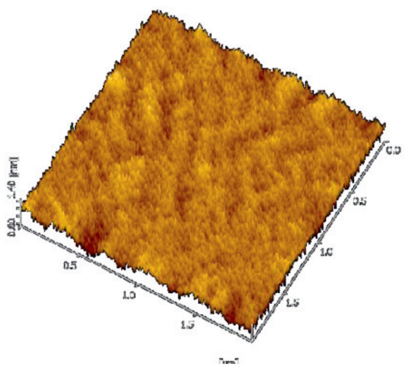


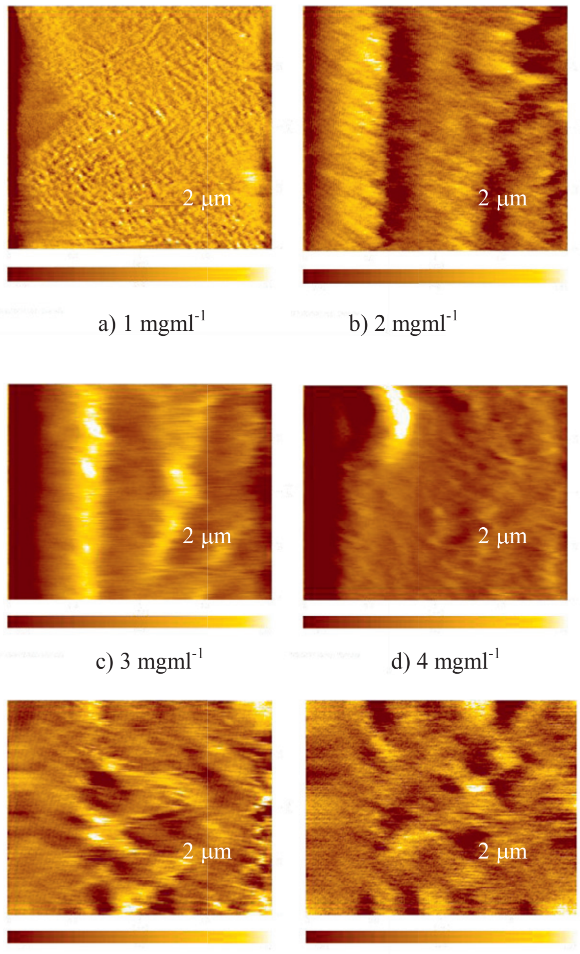
Fig. 7. 2μm ×2μm AFM images of MEH-PPV film spun at 6k rpm speed with solution concentration of 8 $mgml^{-1}$.

Table 1. grain size,mean surface roughness and root mean square from afm for figure 4 to 7

Spin Speed (krpm)	Grain size (nm^2)	Mean Surface roughness (Ra, nm)	Root mean square (RMS, nm)
1	1677±189	0.037 ± 0.009	0.021 ± 0.005
3	1635± 661	0.020 ± 0.004	0.009 ± 0.002
4	1295±269	0.030 ± 0.0	0.020 ± 0.005
6	713± 125	0.064 ± 0.016	0.035 ± 0.009

Chen et. al reported [1] that improving the surface morphology of the MEH-PPV layer would improved the performance of the device. Table 1 also tabulates information on the surface roughness of the film when the spun speed increases from 1k to 6k rpm. It can be seen that when the spun speed increases the grain size of the MEH-PPV decreases significantly. At spun speed of 6k rpm the grain size MEH-PPV of the film is the most homogenous with the smallest grain size ~713.2±0.1 nm^2. This is probably due to the MEH-PPV film is less entangled when film is spun at higher speed. The surface roughness has no specific relation with the increase in the spun speed.

The surface topography of each film spun at various speed is clearly not similar from one another. The three films spun at spin speed of 1k rpm, 3k rpm and 4k rpm have features of clumping whereas the film spun at 6k rpm, it shows features of zig-zag stripe-like structure [10]. However, for the image at 4k rpm, the clumping is quenched and it probably shows that the polymer tends to extend. The stripe-like structure is aligned almost in the same direction. Figure 8 represents AFM images of MEH-PPV spun film obtained from chloroform solution at various concentrations but spun at the speed 4k rpm. All the images cover an area of (2×2) μm^2, but the color height scales are different from one to the other. The images show that the final morphology of the MEH-PPV film changes significantly when the solution concentrations used to produce the MEH-PPV film increases.



a) 1 $mgml^{-1}$ b) 2 $mgml^{-1}$

c) 3 $mgml^{-1}$ d) 4 $mgml^{-1}$

e) 5 $mgml^{-1}$ f) 8 $mgml^{-1}$

Fig. 8. 2μm ×2μm AFM images of MEH-PPV film spin at 4k rpm by using various solution concentrations

The result of surface roughness and grain size obtained from Figure 8. The relationship between grain size to concentration and surface roughness to concentration were shown in Figure 9 and 10 respectively. From Figure 8, the net of polymer chain is clearly seen when the polymer solution concentration is increased. At solution concentration of 1 $mgml^{-1}$ the polymer chain on the film is very far and isolated from each other. When the solution concentration increases, the polymer chain becomes closer to each other. At solution concentration of 2 $mgml^{-1}$, the stripe features of polymer chains are very small but at 3 $mgml^{-1}$, the stripe is clearly seen and the size is larger. As it is known that, polymer chain is in the region below the CLA. The entanglement of polymer chains is expected not to occur. However, when the solution concentration increases to 5 $mgml^{-1}$ and 8 $mgml^{-1}$, the clumping of polymer is clearly observed.

Figures 9 and 10 show the grain size and surface roughness against the solution concentration used to produce the MEH-PPV film. The highest grain size and surface roughness is displayed by MEH-PPV film produced from solution concentration of 3 $mgml^{-1}$. In the c<CLA region, ideally there trend of grain size and surface roughness of the spun MEH-PPV film with the solution concentration as reported by Shi et al [11]. The image produced from solution concentration of 1 $mgml^{-1}$ is quite smooth and the pattern is slightly different from the image produced from solution concentration of 3 $mgml^{-1}$. If height scales for 1, 2 and 3 mgml-1 solution concentration of the films are compared, bumps ranging from 2.21-2.54 nm height are observed which suggest a very large tangled region of the polymer chain. The images in Figure 8 (d) to (f) are quite consistent. It suggested that the formation of the conjugated polymer aggregation by interpenetration of adjacent chain in solution survives the spin casting process and it persists into the film [1]. All images do not provide information on conformation of individual chain in the films.

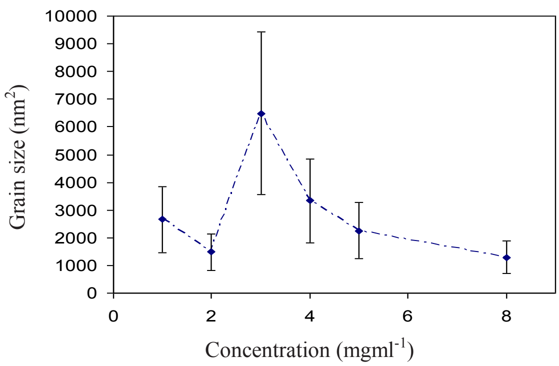


Fig. 9. Grain size against solution concentrations of MEH-PPV spun film at 4k rpm

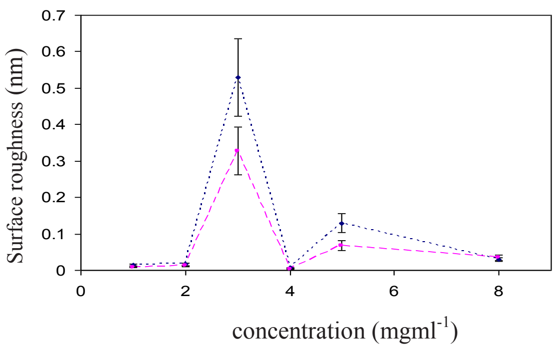


Fig. 10. Surface roughness against solution concentrations of MEH-PPV spun film at 4k rpm

4. Conclusion

Conjugated polymer strongly effect by the processing parameters such as spin speed, concentration of solution, types of solvent and substrate. The independent results was shown due to working regime of this project is below CLA region. From the SEM images, the homogeneity of the films was in good condition, however the aggregation of the polymer based on AFM images shows the independent pattern when the concentration of the solution and spin speed was varied. The surface roughness and grain size analysis from the AFM images indicate that the highest value of both analysis significantly seen at concentration between 2- 4 $mgml^{-1}$.

Acknowledgements

The authors would like to thank the Government of Malaysia for providing research Grant under IRPA RMK8 : 09-02-03-1028 ,Vote F and UniMAP.

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